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Report of the Materials Research Council (1977)

August 1977

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ARPA Order No. 2341

THE UNIVERSITY OF MICHIGAN 1817

6 REPORT

OF

THE MATERIALS RESEARCH COUNCIL

(1977)

10 M. J. Sinnot

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12 115 p.

15 MDA9Ø3-76-C-Ø25Ø, ARPA Order-2341

14 Ø14521

ARPA Order Number: 2341/3
Program Code Number: 6D10
Contractor: The Regents of The University of Michigan
Effective Date of Contract: 1 July 1977
Contract Expiration Date: 30 June 1978
Amount of Contract: $300,000
Contract Number: MDA903-76-C-0250

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INTRODUCTION

This report is a summary of the activities of the Materials Research Council during its annual Summer Conference held in La Jolla, California, during the period July 5-29, 1977. (over) A more complete presentation of the technical papers, workshop reports and memoranda generated by the Council will be prepared and issued later in the contract year.

The Materials Research Council was organized by the Materials Science Office of the Defense Advanced Research Projects Agency to assist them in examining potential future materials problem areas of the Department of Defense. It is not directly concerned with current problems, although it has and will continue to work on these when it can be of assistance. Its primary function is to look beyond the current problems to those of the future and to suggest possible studies that will insure that the necessary science base and preliminary engineering feasibility studies are in place to support later engineering and system development.

The membership of the Council is made up of ceramists, metallurgists, chemists, physicists and engineers whose common interests lie in materials science or materials engineering. This meeting of the Council was the tenth year of operation and over this period this diverse group of scientists and engineers

have developed into one of the most knowledgeable and versatile consultant groups in the Country.

Since most of the Council membership is drawn from the academic community, their early exposure to emerging materials problems results in their prompt transfer, via their graduate students, into active research programs. Support of these programs comes from several sources, not just the Department of Defense. NSF, ERDA, Industries, Universities and Technical Associations are all represented in the support of these research programs. The range of these programs is very broad since it covers all of the topics that have been examined by the Council over the last several years. (cont fr p1) Currently work is going on in large space optics, non-destructive inspection, laser materials, non-equilibrium alloy structures, strong optical fibers, composite material penetrators and structural ceramics.

While the Council has considerable expertise in many areas, it draws heavily from the science and engineering communities for consultants, assistance and advice. These come from government agencies, industrial laboratories, not-for-profit institutions and from universities. Visitors who have a special interest and capabilities in the areas under consideration by the Council are encouraged to attend and take part in the briefings and discussions that make up part of the Summer Conference of the Council. Visitors have included NSF and NBS personnel, representatives of the basic research offices of the three services; AFOSR, ARO, and ONR and other DoD research and

development groups such as NRL, AMMRC, AFML, AFWL, NSRDC, NSWL, etc. These service personnel perform a particularly valuable function since they have an intimate knowledge of on-going current research and can relate it to the advanced research concepts under consideration of the Council to the benefit of both groups.

PROJECT ORGANIZATION

The technical direction of the Materials Research Council is delegated to a seven-man Steering Committee chosen to represent the various disciplines of the Council membership. Membership on the Steering Committee is usually for a period of three years with replacements made each year.

The functions of the Steering Committee are:

a) Work with ARPA-MATS to select problem areas for consideration by the Council.

b) Select Council members, specialists and consultants to work with the Council.

c) Structure, direct and evaluate Council activities.

d) Participate in project management.

The current Steering Committee is as follows:

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There are many people qualified for Council membership but budgetary considerations limits the numbers to 20-25. To obtain a greater flexibility of membership, a recent policy was instituted where some of the Council members are asked to go on an inactive status and new members are added. Some members, because of other commitments, elect to be placed on the inactive list. Inactive members are usually recalled to membership as the Council moves back into their areas of expertise. The current inactive list of Council members is as follows:

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ORGANIZATION OF THE SUMMER CONFERENCE

The principal function of the Materials Research Council is to provide ARPA with a variety of services which bear on the development and use of materials in defense systems. The vehicle for providing these services is the Summer Conference which is a one month summer study meeting.

During the summer meeting the Council not only carries out research of an analytic nature, but also holds conferences and workshops devoted to themes of mutual interest to the Council and ARPA with a balance being sought between themes suggested by ARPA and those suggested by the Council. Position papers are prepared after the conferences and workshops, to aid ARPA in judging the pertinence of new programs, in stimulating the

generation of such programs, or in assisting in the evolution of new scientific concepts. A secondary aim is the stimulation of the research efforts of individual scientists and engineers who participate in these meetings. Workshops are attended by Council members, who may not be expert in the subject under discussion, and by a core of experts, usually non-Council members, who are selected and invited by the Steering Committee to lead the discussion. The philosophy under which Council members participate in conferences outside their customary interests is based on the idea that highly competent scientists, even if not experts in that field, can bring fresh ideas to that field by virtue of their competence and the fact that they may not be committed to firm and sometimes controversial points of view.

Several techniques for conducting the summer conference have been implemented during its ten years of operation. Initially the entire MRC membership focused on a few problems presented to them via briefings from the various segments of the Services or DoD agencies. Typical topics covered were: Shock Propagation, Constitutive Relations at High Temperature and Pressure, Composite Materials and Underground Sensing. From this the Council evolved a technique whereby individual Council members were given the responsibility of structuring conferences or workshops that would be of interest to different subsets of the Council. Meetings have been held on such topics as Amorphous Semiconductors, Infrared Optics, Materials in Energy Systems, Structural Ceramics, etc.

Because of continuing interest from year to year of the individual members in certain topics, there is a considerable carry-over from one conference to the next of the various study areas. Over the ten year period, of the order of twenty-five major studies have been carried out in areas such as: Composite Materials, Biomaterials, Laser Optics, Superconducting Materials, Solid Electrolytes, Wear, Erosion, Fracture. From these major studies, smaller groups of the Council have nucleated studies in spin-off areas that are more suited to their particular expertise and they regularly report back to the Council the new developments, refinements in theories, experimental studies, new applications, etc.

Output from the Council appears in three publications. An Executive Summary submitted to ARPA management, a Preliminary Report which gives in summary form the results of the Summer Conference and a Final Report, issued later in the year, which contains all the written output of the Council. Much of the Final Report consists of technical papers ready for publication in appropriate journals. The balance are preliminary reports and memoranda generated primarily for distribution within the Council and to its consultants. They serve to stimulate discussion since they are initial position papers and present tentative unrefined concepts and ideas. Their distribution is restricted since they do not represent a unanimous or even a consensus opinion of the Council. They are available on request to the Project Director subject to the author's release.

For the 1977 Conference, ARPA requested some additional output. The members of the ARPA Staff submitted questions and/or inquiries to the MRC members asking for their opinions or advice on specific topics of interest to the program managers. Subcommittees of the MRC were constituted to address the questions and prepare answers. These questions and the proposed answers were then discussed by the MRC as a whole and final answers were prepared. These were then submitted to ARPA at the close of the conference in the form of an Executive Summary.

SUMMER CONFERENCE - 1977

In preparation for the 1977 Conference the Steering Committee met in Washington, D.C., in February with the staff of the DARPA Materials Science Office. At that meeting ARPA-MATS arranged for a series of briefings in the following areas:

- Large Optic Materials (HALO, HELO)
- Optical-Microwave Devices
- UV-Visible Laser Optics
- Chemical Laser Nozzle Materials
- Fiber Strengthened Penetrators
- High Impact-High Pressure Materials Behavior

After these briefings the Steering Committee discussed various problem areas suggested by MRC members for consideration by the Council at the 1977 meeting.

The total number of suggested problem areas was far greater than the number that can be addressed at a single summer conference meeting. This is not an uncommon occurrence and it was the feeling of the Steering Committee that to accommodate

a broader spectrum of topics our mode of operation should be changed. In place of the usual two or three day briefings involving consultants and contractors the presentations at most of the conferences would be limited to one or two knowledgeable individuals who present the problem and suggested solutions, and then work with the Council members in refining these or examining new or alternate solutions.

For the 1977 Summer Conference two of the regular type meetings were scheduled. One on Non-Destructive Evaluation and the other on Rapidly Solidified Powders. The balance of the briefings were to be limited to half-day or single day presentations. With this format the Council felt that more time could be spent in working on problem solutions rather than hearing several somewhat repetitious formal presentations.

The formal program for the 1977 Summer Conference as structured in February by the Steering Committee was as follows:

July 6-8	Non-Destructive Evaluation (Thomson-Krumhansl)
July 7	Structural & Materials Considerations Large Space Optics (Hucke)
July 8	Fluorine Reactions with Ceramic Materials (Margrave)
July 11,12,13	Rapidly Solidified Powders (Cohen, Hirth, Hucke)
July 14	Laser Shock Effects (Thomson)
July 15	Fiber Reinforced Penetrators (Budiansky)

The MRC member or members responsible for structuring the presentations are indicated above.

The actual agenda at the Summer Conference was expanded between the planning meeting in Washington and the convening of the group in La Jolla in July. The conference site was used by ARPA to meet with contractors, to review programs, and to co-ordinate joint efforts with other agencies such as AFML, Aerospace Corporation, ERDA, et.al. Most of these meetings were attended by Council members who have an active interest in the areas that were under consideration.

The following is a topical list of the meetings that were held. This is then followed by the more detailed agenda and a list of attendees at the meeting. For those meetings held under MRC sponsorship, a summary is presented by the MRC member or members who had arranged the presentations.

FINAL AGENDA OF 1977
Materials Research Council
Summer Conference

July 5	Program Review of DARPA Materials Science Office A. L. Bement
July 6	Strong Optical Fibers H. E. Rast, NELC
July 6,7,8	NDE Workshop R. Thomson, J. Krumhansl, MRC
July 7	Electro-Optical and Acousti-Optical Materials R. Reynolds, ARPA
July 7	High Altitude Laser Structural Materials W. Cuneo, ARPA, E. Hucke, MRC
July 8	Fluorine Resistant Materials J. Margrave, MRC
July 11,12,13	Rapid Solidification Technologies M. Cohen, J. Hirth, E. Hucke, MRC

July 14	Laser Induced Shock Effects (Joint with JASON) ERDA, Thomson, MRC
July 14	Space Applications - Metal Matrix Composites A. Bement, ARPA
July 15	Fiber Reinforced Penetrators B. Budiansky, MRC
July 15	Ceramic Horizons A. Evans, MRC
July 15	IR Window Program Review H. Winsor, ARPA
July 20	UV-Visible Laser Component Review H. Winsor, ARPA
July 27	Review of ARPA Questions MRC-ARPA
July 29	Review of MRC Studies MRC

MATERIAL SCIENCE OFFICE PROGRAM REVIEW

Dr. A. L. Bement of the Materials Science Office of ARPA opened the conference with a discussion of the current programs being supported by his office and the objectives of those programs. He followed this with a discussion of the various new research areas that were being considered and emphasized that these undertaken only after a technical assessment is made to determine the feasibility, risks and payoffs.

A series of inquiries were presented to the Materials Research Council by ARPA and they were requested to consider these during the Summer Conference and give their responses at the close of the meeting. This procedure was initiated in order to improve and strengthen the communications between Council

members and the members of the Materials Science Office. To still further improve this linkage he suggested that year-around seminars/workshops be scheduled dealing with specific thrust areas that are of interest to ARPA.

STRONG OPTICAL FIBER REVIEW

During the 1976 Summer Conference a joint workshop with the Navy Electronics Laboratory Center (NELC) was held. This same group scheduled a Program Review at the 1977 Conference. The agenda for that meeting is given below.

Event	Speaker
Introduction	B. Bendow
Mechanical Behavior of Optical Fibers	K. Kalish
High Strength Fibers	D. Pinnow
High Strength Fibers	M. Maklad
Strength of Coated Silica Fibers	P. A. Turner
Strengthening of Optical Fibers by Compressive Cladding	P. Macedo
Fractography/Strength Testing	S. Freiman/H. Rast
Strong Fibers	R. Maurer
Round-Table Discussion	Attendees

ULTRASONIC SCATTERING AND THE "INVERSE PROBLEM"
IN NON-DESTRUCTIVE TESTING

R. M. Thomson

INTRODUCTION

A workshop to review the technical difficulties inherent in the inverse problem in NDE was held at the MRC Summer Meeting at La Jolla on July 6-8. The list of attendees is attached. The major purpose of the workshop was to attempt to come to grips with the prospects for specifying as completely as possible a scattering defect in a material from measurements of scattering, diffraction, attenuation, etc., of ultrasonic waves in the material caused by the defect. Inevitably, the workshop led to a general discussion of the state of present theories of ultrasonic interactions with defects in matter, and to an attempted assessment of the potential for future developments. We shall present here the highlights of this discussion. The subject is most naturally broken into three parts, the long wave limit, short wave limit, and surfaces. Our final section is an overall conclusion, with suggestions for future attention.

LONG WAVE LIMIT

The general breakdown into long and short wave limits follows most easily from a look at the equation

$$u_s = \hat{r}_i\hat{r}_j \; f_j(\alpha) \; \frac{e^{i\alpha r}}{r} + (\delta_{ij}-\hat{r}_i\hat{r}_j) \; f_j(\beta) \; \frac{e^{i\beta r}}{r} \tag{1}$$

the first term is the longitudinal scattering, and the second is the transverse part. $\hat{r}_i$ is the unit vector to the point of observation, α and β are the longitudinal and transverse k-vectors of the scattered wave, respectively. f_i is the scattering vector which gives all the information on the scattering amplitude. It can be given for a scattering volume (e.g., precipitate particle), or a scattering surface (e.g., crack) as follows

$$\begin{aligned} f_i(k) &= \frac{k^2}{4\pi\rho\omega^2} \int dV'(\omega^2\delta \; u_i + ikr_j\delta c_{ijk\ell}\varepsilon_{k\ell})e^{i\underline{k}\cdot\underline{r}} \\ f_i(k) &= \frac{k^2}{4\pi\rho\omega^2} \, c_{ijk\ell} \int_{S^+} dS'(ikr_j \; n_k^+ \; \Delta u_\ell)e^{ik\cdot r'} \end{aligned} \tag{2}$$

The first equation is for a scattering volume V', and the second for a scattering surface, where the integration is taken over the upper portion of the surface. $\delta\rho$ is the perturbation in mass in the volume, $\delta c_{ijk\ell}$ is the perturbation in elastic constants, Δu_ℓ are the displacement discontinuities on the surface, ω is the frequency, and $\varepsilon_{k\ell}$ are the strain components.

In the long wave limit, the wave length is long compared to the size of the scatterer, and the phase shift over the volume or surface scatterer is neglected. Thus, $e^{i\underline{k}\cdot\underline{r}'} \to 1$. In this limit, the strain and displacements in the scatterer can be obtained for simple crack and inclusion shapes, and in particular

for ellipsoidal inclusions in the static limit. Eshelby has published solutions for constant stress, which can be used as a basis for obtaining the elastic solution. Likewise, in the crack case, the displacement discontinuities can be related to the stress intensity factors for simple shapes. Circular crack shape scatterers have been worked on, and theorems for the average stress intensity factors are being obtained for general shapes. Finally, the importance of a formal investigation of Eqs. (1) and (2) for the number of parameters which are necessary to completely specify the scattered wave in the long wave limit was recognized at the workshop. In subsequent work by MRC members Kohn and Rice, it was found that the number of independent parameters in the long wave limit is 22. Further, they have shown that from a simple longitudinal to longitudinal scattering experiment, one can obtain unambiguously the total excess mass contained in a defect volume. Further, from measurements of the scattering of incident longitudinal and transverse waves into longitudinal outgoing waves one can obtain 6 useful parameters which may be interpreted in terms of an equivalent ellipsoidal void or an equivalent ellipsoidal non-deformable inclusion.

From the experimental point of view, a complete inverse determination will require experimental discrimination between the three independent polarization vectors. To some extent this is provided in the time domain because of differences in velocity between transverse and longitudinal signals, but discrimination

between transverse polarizations normal and parallel to the plane of the scatterer may also be required, for example, in the crack case to give orientation information.

Generally speaking, the long wave case has now received extensive attention. Further work is required on the application of the theoretical results in the light of experimental and practical constraints, and on the significance of the independent parameters in terms of special shapes of importance. Also, the possibilities of marrying these results to the empirical learning approach should be investigated. Thus, it is now appropriate to consider ways and means to convert this understanding into practical use.

SHORT WAVE LIMIT

In one respect, the short wave limit is the simple one, experimentally, because it leads to simple ray theory and imaging. Thus, one simply "sees" the object doing the scattering with some similitude to the real object. This is the ultimate goal, for example, in such techniques as sonic holography or imaging systems using arrays and/or scanning.

Typically, however, these techniques do not provide all the information one would like, because, for example, specular reflection from a crack tilted at some general angle of the receiver may not be detected by the system. In this case, one does, however, detect diffraction effects at edges, etc. In some ways, these diffraction effects are all the more important because they are sensitive to local curvature and sharp corners

which the simple image does not show. In addition, waves which convert into surface waves on the scattering object, circumnavigate the object, and become reconverted into scattered waves, create interference effects with the directly scattered beam. Thus, phase differences create special interference effects in the scattered amplitude, and "resonance" effects in the frequency dependence of the scattered amplitude. Both are observable, and yield important information about the defect.

In particular, a geometrical diffraction theory should be developed for circular and elliptical cracks for arbitrary polarization and incidence angle. The theory should include both the direct scattering as well as waves converted to and from surface waves on the crack. From this theory, amplitude and phase variation as a function of scattering angle and frequency should be generated. A feature of the short wave limit of particular interest is the existence of "caustics", or singular directions of high intensity scattering. For example, the forward scattering of a circular opaque object in both optics and acoustics is of such a character. For an elliptical scatterer, the forward caustic is the evolute of the curve bounding the opaque object.

Although ray theory applied to two dimensional cracks of simple shapes should be relatively straightforward, one can also apply it to simple three dimensional shapes representing both voids and inclusions.

Obviously, the inverse problem in the short wave limit is at the same time both simpler and more complex than the long wave limit. It is simpler when working in the imaging regime where the image is a direct representation of the object - it is far more complex when working in the diffraction regime, where a variety of involved phenomena occur.

The inverse problem in the short wavelength limit has much in common with the problem of imaging. In the inverse problem, an attempt is made to mathematically determine not only the shape of a volume flaw, but also its material properties, e.g., δc_{ijkl}, etc. A typical imaging system is basically a hardware implementation of such a software mathematical inversion procedure. It would be useful to determine analytically the relation between the two procedures, and find how much can be learned from these two very different ways of attacking the inversion problem. One question is, for instance, the determination of how much information other than the shape and size of a flaw can be obtained by proper processing of the signals from an imaging system. Another is to determine whether image processing is useful in the low frequency limit. A third is to learn whether the mathematical inversion procedures presently used are optimum, or whether by following procedures, such as those developed in the field of x-ray and acoustic tomography, more accurate information on material properties and sizes of flaws could be obtained.

Variational principles and special discretized techniques have been developed by members of the MRC for application to the scattering problem. It appears that the variational method of Kino may have application in guiding the numerical calculation of scattering from complex objects. The discretized method of Montroll is a technique which is designed from the outset for setting up on a computer and could prove very useful in obtaining qualitative information on how complex shapes can be expected to behave as scatterers.

Both techniques may also have application in covering the intermediate regime between the short wave along wave limits. Very little has been done so far to tackle this technically important situation, covering many typical flaw sizes. The only approach presently available to deal with the regime is to extrapolate curves obtained from the high frequency and low frequency scattering analysis.

SURFACE DEFECTS

Surface defects constitute one of the more important practical applications for NDE, but both the experimental as well as the theoretical situations are not as well developed as for defects in the bulk. For example, the crack emanating from a fastener hole is a special geometry not analogous to any of the elliptical or ellipsoidal special shapes considered previously.

At the workshop, however, a very interesting proposal was made by Gomer and Richards for experimental detection of surface flaws. One suggestion is to generate bubbles in a fluid

film covering the surface of a flawed material. A second is that the standing wave pattern generated by reflected surface waves from a surface defect should be observable on the surface near the defect, and that various laser techniques might be used to observe them. These suggestions are sufficiently novel and straightforward that they should be pursued.

A start has been made on the low frequency theory of surface wave scattering from a penny-shaped crack by Auld and Kino using an approach based on the reciprocity theory. Much remains to be done and should be done to develop theories analogous to those for bulk wave scattering which are suitable for use with Rayleigh waves, as well as the waveguide mode of materials of finite thickness.

CONCLUSIONS

The main purpose of the workshop was to assess the possibilities for specifying the important parameters of material defects from scattered ultrasonic waves. It appears that in the long wave limit, a partial inverse characterization is now achievable in the near term, and should be pursued. In the short wave limit, simple imaging is being intensely pursued, experimentally, but the whole domain of diffraction and resonance effects is yet to be adequately developed both experimentally and theoretically.

With this stage of general background understanding, an opportunity exists ultimately to combine aspects of long wave scattering, short wave imaging, and the empirical computerized

training approach into an integrated system for flaw characterization. The demonstration of such a system would be at once a large stimulus to the NDE industry and a justification of the whole approach of quantitative NDE. Explorations of technical ideas for incorporation into an eventual test bed could begin now, and with the stimulus of the fast progress in this field, over the next year, could begin to crystallize into a program for a test bed. Other applications are proposed by Kino in other parts of this report.

NDE WORKSHOP

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SUMMARY OF MEETING

ON

STRUCTURAL MATERIALS FOR LARGE OPTICAL SYSTEMS IN SPACE

E. E. Hucke

Considerable interest has been generated in designing large optical systems of extremely high quality. A short meeting to explore advanced materials for mirrors was held on July 7, 1977. A list of the participants is appended. Such mirrors must be shaped on the ground, space erected and held to the final very close dimensional tolerances by adaptive actuators. An analysis of the materials properties required by the systems choices was given by Cuneo of DARPA. He gave an ordered list of desired materials properties and asked for a major improvement in any one property as a criterion of success for materials to be employed in future systems.

The current materials and methods of fabrication were discussed by Levenstein. In addition, he presented some thoughts on advanced materials and fabrication schemes.

A spirited discussion of microstructural features for obtaining low expansion in glasses was led by Lewis.

The present state of application of graphite-epoxy and graphite-carbon composites for mirror supports was presented by McNamara.

STRUCTURAL AND MATERIAL CONSIDERATIONS
FOR LARGE SPACE OPTICS MEETING

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MATERIALS FOR HANDLING F_2/HF AT HT's

J. L. Margrave

INTRODUCTION

Initial orientation comments were provided by Capt. Harry Winsor of the DARPA Materials Science Office and by Dr. Margrave. The goal is to identify those materials which can best be used to handle fluorine and HF in the configurations and temperature-time duty cycles anticipated for the H_2-F_2 and D_2-F_2 laser systems currently under development by the Air Force, Army and other DoD organizations. As a broad guide to evaluation, an ideal material would survive for 10-20 minutes in the presence of gaseous F_2/HF at 2400 K. The ideal material would either be unreactive with F_2/F-atoms/HF or form a stable protective film or erode away at a rate slow enough to meet the requirements. It would also have to be resistant to mechanical and thermal shock, especially the latter, since duty cycles of $\sim$100 seconds at 2400 K could be followed by rapid cool down then a later fast heating back to 2400 K.

Since complex shapes are likely to be needed, the material sought should be easily formed by standard ceramic or metallurgical techniques and it must be stable in the ambient environment, i.e., resistant to oxidation or nitridation by air and resistant to hydrolysis by atmospheric humidity, dew

or rain. Obviously, the high-temperature application requires that the materials have high melting points, high boiling points and low vapor pressures. No stable, volatile ternary gaseous species should be formed at high temperatures.

CURRENT KNOWLEDGE

There are many materials currently known to be satisfactory for handling fluorine at low temperatures and up to ∿1000 K, as listed in Table 1. The cryogenic handling of fluorine at temperatures below 90 K has become routine and the problems are similar to those observed in handling liquid oxygen. Most metals and many compounds do not react with fluorine molecules at temperatures below 50 K. F-atoms can be obtained by UV-photolysis and these are more reactive. Glass and other oxides and various refractory fluorides are satisfactory for dry F_2. Metals like Al, Mg, Cu, Ni and Fe-alloys are also satisfactory at room temperature and below. Ti, Mo, W and Ir are not reactive. Graphite and carbons are quite fluoride resistant.

Rather unexpectedly, there are several hydrocarbon-based plastics which are satisfactory as containers/protective surfaces in the presence of F_2 at room temperature and up to ∿200 C or their melting (softening) points. These include polyethylene, polypropylene, polyvinyl chloride and fluoride, polyvinylidene chloride and fluoride, polystyrene, natural or synthetic rubber, Kel-F and Teflon. All of these materials are potentially oxidizable to CF_4 by elemental fluorine but initially

they form protective films (poly-CF_2 layers) and do not react further unless heated, flashed or exposed to high-pressures of fluorine. Graphite, carbons and even diamonds are apparently protected by a similar fluorocarbon surface coating.

At 1000 K, the useful ranges of the low melting metals and plastics have been exceeded; metals like Cu and Ni and alloys like Monel or Ni-Al alloys are protected by thin layers of stable and relatively non-volatile fluorides (CuF_2, NiF_2, AlF_3); and carbon, graphite and diamond are protected by gray to white layers of the variable stoichiometry compound, CF_x, where $x = 0.6$ to 1.2. Refractory fluorides like MgF_2, CaF_2, CeF_3, etc. are unreactive with F_2, and certain refractory oxides (Al_2O_3, Y_2O_3, UO_2, etc.) are protected by films of non-volatile fluorides or oxyfluorides.

Thermodynamic and kinetic considerations indicate that no solid material will be truly stable in F_2 at 1 atm and 2000 K or higher, especially with high flow rates of reactant gases. There are no binary fluorides which have not melted, and/or vaporized. All elements oxidize to yield gaseous fluorides, exothermically. The CF_x-coating on graphite burns to CF_4-gas. Refractory oxyfluoride films which might be protective are not well-characterized, if they really exist. Thermodynamic and kinetic calculations are only qualitative because of the lack of reliable thermodynamic data and of molecular parameters for evaluating statistical thermodynamic functions for the various high temperature species.

Further details and extensions of these ideas and other concepts were presented by the various participants.

CONCLUSIONS

Practical solutions to the problem of handling F_2/HF at temperatures above 2000 K would appear to be:

1. Design an expendable, sacrificial unit which will be extensively if not catastrophically fluorinated in the use cycle and then replaced.

2. Design an expendable unit but operate at lower temperatures, say 1500 K, for longer life.

3. Continue testing and research to see if

a. Sufficiently stable, refractory, non-volatile oxyfluorides exist to protect oxides when used.

b. The island of reactivity concept will provide a sufficient life-time for Ir or W or Mo or some alloy.

c. There is a super-stable, non-volatile ternary fluoride that can be protective.

The DARPA/DoD programs concerning F_2/HF handling in high-temperature systems are providing excellent kinetic data for F_2/F-atom reactions with various candidate materials (Nordine and Rosner, Yale), excellent computer predictions based on available thermodynamics (Wallace, LASL), and excellent test data on full-scale objects in realistic temperature/composition/flow ranges (Webber, Oak Ridge).

There are some research areas, however, which are not currently active under this program which could significantly

strengthen the thermodynamic predictions, clarify some of the presumed mechanistic details required to explain observed kinetics and lead to new compositions for full-scale test samples. Suggested areas for additional work include:

1. Synthesis and characterization of several oxyfluorides,

   a. AlOF

   b. YOF or LaOF

   c. $TiOF_2$ or UOF_2

   d. etc.

2. Spectroscopic studies of a broad group of MF, MF_2, MF_3* species by matrix infrared/Raman/ESR techniques and by laser fluorescence to provide molecular parameters, magnetic properties, etc.

3. Calorimetric studies by direct combustion in F_2 to provide reliable data in IrF_6, PtF_4 and other reference compounds.

4. Measurements of surface properties, especially the emissivities of fluorides (NiF_2, CuF_2, AlF_3, CF_x, etc.) to allow more reliable establishment of operating temperatures.

5. Formation of composites having various combinations of properties:

   a. CaF_2 in porous graphite (hydroxide wetting agents).

   b. Ni/Al/C powdered and formed with C-rich outer layer.

   c. Ir-coating on graphite substrate.

   d. Mg/Al/C powdered and formed with C-rich outer layer.

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*M = Mo, W, Nb, Ta, Ir, Re, Rh, Pt

6. Studies of $ZrPt_3$, $HfIr_3$, etc. for possible fluorine resistance.

7. Search for new ternary fluorides in these phase diagrams:

   a. NiF_2/AlF_3 system

   b. NiF_2/YF_3 system

   c. NiF_2/CaF_2 system

   d. nUF/UF_g where y = 4,5,6 and n = 1 or 2

   e. CaF_2/ZrF_4, ThF_4 or $UF_4 \rightarrow CaMF_6$

   f. CaF_2/WF_4, WF_5 or $WF_6 \rightarrow CaMF_{6,7 \text{ or } 8}$

FLUORINE RESISTANT MATERIALS FOR HIGH TEMPERATURE APPLICATIONS

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REPORT ON RSP MEETING

M. Cohen, J. P. Hirth and E. E. Hucke

SUMMARY OF PROCEEDINGS

A three-day meeting for the review of the progress in current RSP programs, delineation of new small-scale rapid solidification schemes, and consideration of consolidation problems was held July 11 to 13. A list of invited participants and the program are appended. Several technical papers, extended abstracts, and technical notes as well as conference highlights are presented separately.

The continued and expanded interest by ARPA in the possibilities of RSP were discussed by van Reuth. The original goals for application of this technology to superalloys in gas turbines are now well within sight of realization. There is expanded ARPA interest in providing the research and development community with small amounts of diverse alloys, extension of RSP to specific aerospace aluminum alloys, optimization of processing to final shapes and properties, and novel methods for achieving high cooling-rate structures.

Hirth reviewed the fundamentals of solidification with special attention to the regime of high undercooling. His calculation from the fundamental homogeneous nucleation theory are in quantitative agreement with the observed occurrence of segre-

gation-less microcrystalline freezing. The achievement of this morphology, now found by several investigators in diverse systems, may well be the most significant benefit deriving from RSP.

Further discussion of the range of relations possible between cooling rate during solidification and both primary and secondary dendrite arm spacing (DAS) was presented by Mehrabian. He emphasized that only when the same alloy with the same morphology is being compared can the DAS be used as a good estimate of cooling rate. In reviewing heat transfer calculations, Mehrabian concluded that only under very rapid heat transfer ($h>1$ cal $cm^{-2} sec^{-1} °C$) can there be significant temperature gradients within the droplet prior to solidification. Such conditions however may easily be seen to give duplex morphologies, i.e., dendritic, cellular, microcrystalline. His calculations of heat flow during laser melting and freezing confirmed the possibilities of obtaining very rapid, controlled solidification. This method gives the possibility for changing the average cooling dramatically, but the liquid temperature-gradient to growth-rate ratio G/R is not very high nor selectable over a wide range. The structures to be expected under laser treatment of a given alloy are not expected to be the same as that for other RSP schemes of similar cooling rate.

Lawley presented data on the effects on final properties derived from the differences in the powder compaction variables. His discussion made clear that in many alloys optimum properties for toughness and fatigue require more than just full density,

and will come only after optimizing the flow conditions in compaction, e.g., obtaining substantial shear deformation and sliding between the particles.

The various rate laws covering the densification of metals and ceramics were reviewed by Coble. The densification and structural evolution may be controlled by any of a very large number of paths. For most sensitive applications the last stage of densification is the most important and is likely to be dominated by the exogeneous inclusions. Clean-room techniques appear essential in most cases, but one example of satisfactory air-powder making of aluminum was presented later in the conference. Coble emphasized the need to study transient effects during densification since commercial processes all involve substantial heat up times. Present state-of-the-art hot isostatic pressing (HIP) capabilities would appear adequate for metals of interest even without achieving superplastic flow provided adequate time is allowed for some diffusional flow.

The results obtained to date in the Pratt-Whitney RSP program were reviewed by Cox. Powder yields at rates adequate ($\sim 10^5$ K/sec) to give either very fine DAS or microcrystalline growth have been achieved at high production rates. Consolidated properties including low temperature strength, ductility, low cycle fatigue, stress rupture and high temperature creep, have equaled or substantially exceeded the state of the art for Ni-base superalloys. Cox emphasized the need for avoiding powder contamination prior to reconsolidation. He also presented

interesting results showing substantial non-equilibrium solubility induced by RSP in the Ni-Al-Mo system.

Bloembergen stressed that (in the range proposed for melting) laser coupling to metals was strictly a heating effect, where for almost all materials the heat is deposited in a layer about 200Å thick. While this method is capable of yielding easily computed thermal history, it is essential that control of the laser beam power be within ±10% and that surface contamination with dust be avoided. If not, surface vaporization causes plasma formation which cuts beam absorption drastically.

The excellent possibilities for producing amorphous layers, extended solubilities, and epitaxial growth layers by way of laser glazing were discussed by Kear. Breinan then described layer glazing which extends laser glazing into building three-dimensional pieces by using multiple passes with material added. Unusual structures in superalloys and Co-TaC could be obtained at deposition rates ranging from 0.2 to 1 in^3/min.

Gnanamuthu discussed a laser surface melt alloying process where high dilution of the added alloy with the base metal is sought. Rather thick (∿2mm) layers of high melting point on low melting metals have been produced, e.g., Si on Al and WC on steel.

A very fine (∿15μm) air atomized powder of Co, Cr modified 7000 Al-base Zn-Mg-Cu alloys was used to obtain an outstanding set of properties. Otto showed how these alloys

after optimum processing would yield, at equal stress-corrosion cracking susceptibility, significant improvements in strength, toughness, and fatigue resistance of the state-of-the-art high-strength aluminum alloys. The mechanisms responsible for these improvements are not fully understood. Complete optimization of chemistry and processing remains to be done even though the current materials are now available in sizes ranging up to 3000 lbs.

Another approach to RSP aluminum alloy development was described by Lewis. The aim of this program is for an improved Youngs modulus to density ratio by obtaining very fine dispersions in Al-3% Li alloys.

Cox discussed several alternate means of obtaining high cooling rates employing variants of rotary atomization. These methods are designed for flexible alloy change-over and can yield one dimensionally thin materials ($\leq 5 \mu m$) achieving cooling rates $>10^6$ K/s by splatting the atomized droplets against cooled surfaces. The first method involves off-center pouring against a fully cooled disk atomizer, while the others use a centrifugally produced droplet spun out against a cooled roll or counter-rotating ring.

Perel described a method of breaking up a liquid stream into very fine particles with the aid of a strong electrostatic field. In this method, very fine particles (0.1 to $1 \mu m$) are typically made. Cooling rates are high ($\sim 10^5$ K/s) due to radiation alone at this small size. The electrostatic field is used to collect the particles and could be used to splat quench. The

method can produce only small amounts of material but is potentially flexible in handling alloy changes.

Cline reviewed progress in the use of strong shock waves for the consolidation of metallic and ceramic powders. Provided that adequate momentum traps are used to control the unloading stress waves, it is possible to consolidate fine powders into uncracked fully dense rods and tubes of many materials such as boron, Al, Al_2O_3, and sialons. He showed an example of welded strips of metallic glass retaining the amorphous state. This result gives encouragement toward the aim of making three dimensional bodies from shock-consolidated amorphous metallic powders.

The results of melting and freezing a central portion of a 303 stainless steel ball under rapid shock loading were presented by Sandstrom. While no detailed structural measurements or freezing rate data were available this result establishes the possibility for calibrating structure vs. cooling rate curves at very high rates.

In many of the RSP materials produced by disk atomization, a mixed morphology has been detected. Patterson discussed possible mechanisms for this structure and showed how directional effects can frustrate efforts at determining cooling rate from measurement of DAS. He also showed an example in which, at a given cooling rate the microstructure was significantly altered merely by changing the carbon content of a Ni-based superalloy.

Buckley suggested the possibilities of in-line inspection of HIP parts by sonic imaging techniques. In Ti alloys the initiation of fatigue cracks is most often associated with inclusions. Eylon discussed the implications and requirements for controlling such foreign material.

Clark showed examples where exceptional fatigue and fracture toughness were obtained in RSP Ti alloys even with the known presence of W inclusions in the starting material, and when consolidation was carried out with HIP only.

The progress in making useful shapes and in developing low temperature ductility in TiAl and Ti_3Al materials was summarized by Lipsitt. Significant progress in the case of Ti_3Al was made by adding Nb, W, Zr, and Hf and in the case of TiAl by adding V for ductility and Sb for creep strength.

Tien led a discussion concerning the conditions for G and R required to suppress dendrite freezing in superalloys.

SOME HIGHLIGHTS

The Pratt & Whitney rotary-atomizing process appears to be reaching practical limits on attaining small particle sizes and high heat-transfer coefficients. Even with disk-spinning at 60,000 rpm (instead of the previous 25,000 rpm) the mean particle size by weight is about 50μm for aluminum and nickel, and about 70μm for iron. The Alcoa air-atomizing process, on the other hand, is giving a mean particle size of about 15μm for aluminum alloys.

A copper-roll splat-cooling feature has been added to the Pratt & Whitney small-scale rotary atomizer, and the resulting product appears to be nondendritic. This finding may indicate a higher order-of-magnitude in solidification rate, approaching complete microcrystallinity. The splatting action seems to enhance the effective heat-transfer coefficient between the liquid droplet and the copper substrate because of the liquid shearing involved; also, the accompanying turbulence in the liquid probably helps increase the heat transfer by adding a substantial convective component to the cooling process. However, the irregular shapes thus produced may have some effect on the subsequent consolidation steps, and should receive due attention from that standpoint.

Questions have arisen concerning the validity of secondary dendritic-arm spacing (DAS) as a measure of the solidification rate. Although linear correlations continue to be found between log DAS and log cooling rate, the quantitative relationship varies significantly from alloy system to system, and even within a given system due to compositional changes, e.g., %C in superalloys. It has also been shown that the DAS may vary considerably from dendrite to dendrite among particles of the same size as solidified in a given run. Such differences appear to be real, even after allowance is made for the way that the observation plane cuts through the dendrites. Still another difficulty is that large dendrites may not exhibit enough secondary arms for adequate measurement; and of course, the DAS morphology

is entirely absent when full microcrystallinity is achieved.

In the light of this situation, a challenge exists to develop new methods for determining the cooling rates experienced by small droplets on solidifying from the liquid state.

As predicted last year, there is now evidence that heterogeneous nucleation plays an important role in favoring dendritic solidification over microcrystalline solidification. However, no definitive information is available yet as to the actual benefits contributed by microcrystalline structures to the final properties of RSP materials.

While superplasticity is undoubtedly desirable for achieving full density in the consolidation of particles, there is evidence that superplasticity is neither necessary nor sufficient for this purpose. In other words, complete densification can be obtained by various creep-deformation modes.

A case has been made for the importance of shear deformation during the consolidation of RSP powders in order to obtain good fracture properties; presumable, rubbing of the particles against one another is helpful in securing good metal-to-metal contact for ultimate bonding. Such deformation is surely at play in the extrusion and creep-forging types of consolidation. However, excellent fracture properties have also been obtained by vacuum hot compaction or hot-isostatic pressing of aluminum alloys. Perhaps deformation of the particles and shearing them past one another are also playing a significant role in this instance as well.

In general, substantial improvements in mechanical properties are evolving through RSP methods. In high-strength aluminum alloys, increased fracture toughness, fatigue strength, and resistance to stress corrosion (both static and cyclic) have been documented. The Pratt & Whitney superalloy goals for room-temperature tensile properties and elevated-temperature creep-rate and creep-rupture properties have been reached or exceeded.

Ni-Al-Mo alloys, with Al contents up to 9% and Mo contents up to 35%, have been rapidly solidified into a single highly-supersaturated phase. On exposure to 2000°F for 200 hours, the expected Ni_3Al-type phase precipitates, but the Mo still remains in solution. This is a striking example of the unusual nonequilibrium structures and phase-combinations that can be attained by RSP.

Shock-welding of 40Fe-40Ni-20B Metglass to steel and to Metglass has been carried out with good bonding. Also, 100% density in the shock-consolidation of Pd-Cu-Si noncrystalline powders has been reached. These advances indicate that three-dimensional shapes of noncrystalline alloys are feasible.

In RSP IN100 superalloy, despite processing in helium, no TIP (thermally induced porosity) was encountered after exposure to 2200°F, unlike other powdered materials processed in helium or argon.

SUGGESTIONS

1. Although impressive progress has been made with superalloys and aluminum there are no reports as yet concerning the

suggestions for catalytic, magnetic and electronic materials.

2. Considerable interest has developed in the nature of the fine powders to be produced by the electrohydrodynamic method. Early consideration of the practical problems to be faced in the handling and consolidation of small batches of metal particles ranging down to 0.1μm in diameter.

3. While the building up of bulk rapidly solidified material via layer-by-layer laser glazing has been demonstrated, careful attention should be given to possible adverse effects of the heat affected zones between layers.

4. It is important to establish techniques for the measurement of heat transfer coefficients for small particles, where surface effects may be important. For example, there is some uncertainty as to whether an appreciable temperature gradient exists within convectively cooled, 100μm diameter, IN100 superalloy powders. If h is 2 cal/cm^2/sec the ΔT surface to center is 30K; if h is 0.5 cal/cm^2/sec the ΔT is $\lesssim$ 1K. A knowledge of h and hence ΔT is important in establishing the dependence of structure (and its predictability) as a function of T and $\partial T/\partial t$.

5. Somewhat related to the previous item, what is the actual cooling rate in small particles? At least one fundamental probe into the 10^9 K/s cooling range seems to be needed. On the basis of the shock frozen sample made at Los Alamos, it is suggested that several more controlled shots be performed on simple alloys in an effort to use this method as a rapid cooling rate calibration.

6. Pratt & Whitney reported degradation of creep properties of IN100 after the seal on "mason jar" powder containers was broken and the jars exposed for a month. This bears crucially on the need to fully inert process or not. Other results imply little degradation with air exposure provided extended outgassing is utilized prior to compaction. Controlled experiments or contamination as a function of time and environment are required.

7. For laser glazed structures, turbulence should be induced to create a more uniform microstructure in the glazed region.

8. An increase in grain boundary sliding with decreased grain size below about 70μm mean intercept was reported to give room temperature ductility to beryllium alloys. This implies grain boundary dislocation (GBD) glide. Transmission electron microscope studies of such alloys would provide useful information on such GBD's and possibly suggest methods for achieving even greater ductility.

9. There is now an urgent need to characterize the fine-scale microstructures being obtained by various RSP methods, both from the standpoint of correlating back to the processing parameters and correlating ahead to the resulting properties. Scanning-transmission electron microscopy appears to be an excellent approach in this connection because of its capability for high spatial resolution, microdiffraction, and microchemical analysis.

10. Air atomization of aluminum powder by sucking metal up into a high velocity air stream produces a high volume of

~20μm medium size fine powder as compared to the ~60 to 100μm powder made by the Pratt & Whitney process. Some effort at atomization of nickel based alloys using both inert gas and air in the Alcoa type process would be interesting to determine whether smaller powders can be achieved. In the air case, the more rapid cooling of the smaller particles would lead to a less deleterious nickel oxide on the particles (compared to spinel or more stable oxides in larger particles) which could be later reduced or reacted by a displacement reaction.

RAPID SOLIDIFICATION TECHNOLOGIES

11-13 July 1977

First Session - Morris Cohen, Chairman

Edward C. van Reuth - DARPA Program on Rapid-Solidification Processing

John P. Hirth - Solidification During Rapid Cooling

Robert Mehrabian - Advances in Solidification Processing

Alan Lawley - Consolidation of Powders; Analysis of Processing/Structure/ Property Relationships

Second Session - Morris Cohen, Chairman

Robert L. Coble - Fundamentals of Consolidation by Hot Pressing

Arthur R. Cox and Joseph B. Moore - Progress and Prospects in the P&W Program on Rotary Atomizing and Particle Consolidation

Third Session - John P. Hirth, Chairman

Nicolaas Bloembergen - Laser/Material Interactions

Edward M. Breinan and Bernard H. Kear - Laser Glazing and its Potential Applications

Daniel S. Gnanamuthu - Laser Surface Alloying and Hardsurfacing

Fourth Session - John P. Hirth, Chairman

W. Lawrence Otto, Jr. - Fracture Resistance in High-Strength Aluminum Alloys by Powder-Metallurgy Processing

Richard E. Lewis and Donald Webster - High-Efficiency Rapidly-Quenched Alloys of Aluminum

Fifth Session - Edward E. Hucke, Chairman

Joseph B. Moore and Arthur R. Cox - Small-Scale Rotary Atomizing

Kenneth E. Vickers and Julius Perel - Rapid Solidification by Electrohydrodynamics

Carl Cline - Shock Consolidation of Powders

Brief presentations were also arranged for this session on an ad hoc basis.

Sixth Session - Edward E. Hucke, Chairman

Continuation of brief, ad hoc presentations

General discussion of status and potential of rapid solidification technologies; new research opportunities

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SHOCK WAVES IN METALS

July 14, 1977

A joint meeting was held with JASON on July 14, 1977. Members of MRC and JASON heard presentations from Los Alamos, Livermore, and Sandia personnel. The meeting was classified.

As a result of that meeting an unclassified meeting was scheduled and held at the MRC conference site on July 26. At that meeting Bloembergen and Gilman presented the results of their analysis of the causes of the resistance to large shock wave propagation in metals. The meeting was attended by MRC members and some representatives of the Los Alamos Scientific Laboratory.

The titles and abstracts of these papers are as follows:

RESISTANCE TO SHOCK FRONT PROPAGATION IN SOLIDS

J.J. Gilman

ABSTRACT

The structure of a strong shock front is modeled using a wall of dislocations whose density depends on the compression behind the front. Motion of this dislocation will automatically change the density of the material and simultaneously relaxes the shear strains that would otherwise exist behind the front. However, the dislocation motion is highly dissipative because it requires atoms in intimate contact to slide over one another.

It is shown that the viscosity associated with the dislocation wall motion is large. It is larger than the viscosity of electron-electron interactions, electron-phonon interactions, or phonon-phonon interactions. Because the dislocations move with the shock front, the viscosity coefficient is proportional to the shock velocity so the viscous drag stress is proportional to the shock velocity squared. This leads to large amounts of drag and to a long relaxation time for transient responses.

THE INFLUENCE OF ELECTRONS ON
THE STRUCTURE OF VERY STRONG SHOCKS IN METALS

N. Bloembergen

ABSTRACT

If a metal is compressed by a factor of six in density (volume reduction ratio = 6), with a temperature rise to $3\times10^5\,°K$ and a shock front velocity $u_{sh} = 10^7$ cm/sec, it is estimated that the density and pressure variation occurs in a layer less than 10^{-7} cm, or about three atomic layers of the uncompressed material. The atoms have essentially a mean free path of one interatomic distance and the momentum transfer is effected in a few atomic layers.

The temperature profile is distinctly different in character, because significant energy transfer ahead of the pressure shock front takes place by electrons which move faster than u_{sh}. The width of the diffusion layer of hot electrons ($\frac{1}{2}\, m\, v_{e\ell}^2 = \frac{3}{2}\, kT$, $v_{e\ell} = 4\times10^8$ cm/sec) into the uncompressed metal is estimated to be

$$\delta_{th} = (v_{e\ell}/v_{sh})\,\ell_{e\ell} = (1 \text{ to } 4)\times10^{-6} \text{ cm}$$

These hot electrons have a collision time

$$\tau_{e\ell} = \ell_{e\ell}/v_{e\ell} \simeq 2.5\times10^{-16} \text{ sec}$$

and impart their energy to the cold electrons in the uncompressed metal. The energy is imparted to the heavy atoms in a time (M/m) $\tau_{e\ell} \simeq 2.5\times10^{-13}$ sec.

It is emphasized that charge neutrality at both sides of the shock front is always maintained. The diffusion of energetic electrons into the uncompressed metal is exactly compensated by a flow of an equal number of less energetic electrons into the compressed metal. There is a contact potential at the location of the shock front, but the characteristic Debye length (0.5×10^{-8} cm) is small compared to all distances considered above. Thus the uncompressed metal melts and vaporizes before the pressure shock front compresses it. The model of hydrodynamic compression should therefore have good applicability.

At the opposite surface of a thus shocked metal plate, a fraction of the layer at the free surface (perhaps with a thickness of 40 to 100 angstroms) may become part of the vapor, because it has been heated in the uncompressed condition above 3000°K. If this effect is to be minimized, it may be desirable to coat the free surface with a layer of a low Z material.

REPORT ON MINI-SYMPOSIUM
ON FIBER-STRENGTHENED PENETRATORS

B. Budiansky and D. C. Drucker

INTRODUCTION

In the spring of 1977, following preliminary tests which indicated promising gains in penetrator effectiveness through the use of fiber reinformcement, DARPA initiated the funding of a program at NRL on the development and evaluation of fiber-reinforced penetrators. A half-day mini-symposium on this program was held on July 15, 1977, during the MRC meeting; the agenda is attached. The list of attendees is also attached.

MEETING SUMMARY

Drs. Hettche and Sanday outlined the kinds of preliminary tests that led to the decision to embark on the DARPA-sponsored program at NRL. Aluminum penetrators reinforced with continuous alumina (FP) fibers (about 55% by volume) achieved, under normal impact, complete penetration of an aluminum plate target that withstood unreinforced projectiles at the same mass, diameter, and velocity. Additional preliminary firings have been even more encouraging, showing better performance of Al-FP reinforced penetrators than conventional steel bullets of equal kinetic energy. A large series of normal-impact test firings involving a variety of matrix and fiber-

reinforced materials is planned. Combinations under consideration include Al-FP, Al-W, Al-SiC, Al-G, Pb-Fp, Steel, Steel-W and Du-W. These combinations cover a range of system moduli, strength, density, and ductility. A few tests involving chopped-fiber and particulate reinforcement are also planned. Dr. Brentnall gave a brief description of problems, solutions, and prospects associated with the fabrication of fiber-composite penetrators. Dr. Gurtman discussed the preliminary results of theoretical analysis of stress and deformation based on elastic mixture theory, indicated extensions to plastic mixture theory, and talked about the kinds of large-scale computations that might be involved in the numerical analysis of the penetrator-target impact problem.

DISCUSSION

It is evident that the fiber-reinforced penetrator is a novel idea that has aroused considerable interest in the penetrator and composites communities. (A fair number of the attendees at the mini-symposium were unexpected participants). Given the somewhat surprising preliminary test results, it is reasonable to undertake the kind of systematic, comparative testing that has been proposed, and to provoke supporting analysis. At the same time, it is disappointing that the fiber-reinforced penetrator was not "invented" until now, if it is as good as preliminary tests seem to show. This can only be the consequence of a real lack of basic understanding of penetration mechanics. Further, this same lack leads to the necessity of a

large variety of tests, whose outcome, at the present time, can not be predicted with any reasonable degree of assurance. Large-scale computer programs, which appear to have received the most emphasis in the quest for theoretical understanding, are no better than the basic constitutive and fracture laws that enter into their formulation, and these remain quite uncertain, especially in composites. We perceive a real need for the development of reasonably sophisticated "engineering" theories of penetration that, while they will not supplant detailed continuum calculations, should become the stock-in-trade of penetration mechanicists, enabling them to assess, design, and develop with more than empirical and experiential insight. (See the note by D. C. Drucker in this volume for an example of this kind of approach). At the same time, rationalization of the basic mechanics of materials within computer codes should receive continuing attention, with the aim of making such codes truly predictive from first (or second) principles, instead of post-hoc tools of limited utility. (See, for example, the note herein by A. G. Evans on failure criteria).

We conclude by noting the obvious need to consider oblique as well as normal impact, at appropriate states during the process of evaluation and development of reinforced penetrators.

MINI-SYMPOSIUM ON FIBER-STRENGTHENED PENETRATORS

July 15, 1977

AGENDA

Introduction - B. Budiansky (MRC)

Overview - L. R. Hettche (NRL)

Testing - S. C. Sanday (NRL)

- Ballistic
- Properties

Fabrication - W. D. Brentnall (TRW)

- Processes
- Problems

Analysis-Mathematical Modeling - G. A. Gurtman (SSS)

Key Technical Issues - S. C. Sanday (NRL)

- Problems
- Prospects

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The following is a listing of reports, extended abstracts and technical notes that have been generated at the 1977 Summer Conference. Complete technical papers will be printed in the Final Report which will be published later in the contract year.

On the Estimation of a Crack Fracture Parameter by Long Wavelength Scattering, B. Budiansky and J. R. Rice

An Integral Equation for Dynamic Elastic Response of an Isolated 3-D Crack, B. Budiansky and J. R. Rice

Thermodynamics of the Quasistatic Growth of Griffith Cracks J. R. Rice

Radiant Energy Dissipation in Crack Propagation, J. R. Rice

Detection of Surface Cracks by Laser Doppler Imaging of Acoustic Wave Patterns, P. Richards and R. Gomer

A Simple Method of Detecting Surface Cracks, R. Gomer

Thermographic Crack Detection, R. Gomer

Dynamic Fracture Criteria for Impact Problems, A. G. Evans

Solid Sources for Elemental Fluorine, J. L. Margrave

High Temperature Kinetics of Refractory Metal Gasification by Atomic Fluorine, P. C. Nordine

Evaluation of High Temperature for Use in Hydrogen-Fluorine Environments, G. W. Weber, L. Kovach, C. E. Holcomb, J. B. Condon

Thermochemical Properties of Metal Fluorine Corrosion Products of Importance in F-atom Combustion Lasers, D. L. Hildenbrand

Data Banks of Thermochemical Properties and Computer Predictions of Performance, T. C. Wallace

The Stability and High Temperature Properties of Refractory Oxynitrides, J. L. Margrave

The Stability of Refractory Oxyfluorides, J. L. Margrave

The Stability of Group IV Nitrofluorides, J. L. Margrave

Study of Material Compatibility with HF, F, and F_2 for Combustion Laser Application, T. C. Wallace, R. C. Feber, W. E. Hanth

The Consolidation of Powders, A. Lawley

Hot Consolidation of Powders, R. L. Coble

Advances in Solidification Processing, R. Mehrabian

On the Significance of Superplastic Flow in Hot Isostatic Consolidation of Rapidly Solidified Powders, R. L. Coble

On the Microstructural Aspects of RSP Powders, M. Cohen

Fracture Resistance in High Strength Aluminum Alloys by Powder Metallurgy Processing, W. L. Otto, Jr.

Observations on RSP Research as Applied to High Strength Steels, M. Cohen

Rapid Solidification by Electrohydrodynamics, J. Perel and J. F. Mahoney

Basic Aspects of Rapid Laser Heating and Cooling of Metals, N. Bloembergen

Controlled Displacement Reactions as an Alloy Design Parameter in RSP, J. P. Hirth

Laser Cladding and Laser Surface Alloying, D. S. Gnanamuthu

The Laser Glaze Process for Segmented, In-Situ Buildup of Bulk Rapidly Chilled Structures, E. M. Breinen, B. H. Kear

Feasibility Study to Develop Structural Aluminum Alloys from RSP, R. E. Lewis

Can NDE Infer the Materials Properties of Defects?, R. Thomson and G. S. Kino

Scattering of Long Wavelength Sound Waves from Localized Defects in Solids, W. Kohn and J. R. Rice

A Comparison of Inverse Methods in the High Frequency Limits of Imaging Techniques for NDE, G. S. Kino

Some Comments on the Application of Geometrical Diffraction Theory to Elastodynamic Problems, J. D. Achenbach

Scattering of Waves by Irregularities in Periodic Discrete Lattice Spaces, E. W. Montroll

The Strength of Optical Fibers, A. G. Evans

A Proposed Technique for Monitoring the Processing of Optical Fibers, G. S. Kino

Statistical Interpretation of Fiber Optical Strength, F. A. McClintock

High Performance Ceramics, A. G. Evans and R. L. Coble

The Suppression of Cavity Formation in Ceramics, A. G. Evans, J. R. Rice and J. P. Hirth

Suggestions for a Molecular Resonance Frequency Standard, W. H. Flygare

The Resistivity of Metallic Liquids and Glasses, H. Ehrenreich

Theoretical Strength and Effective Force Laws for Atoms in Metals, H. Ehrenreich and R. Thomson

Microwave and Infrared Coatings from Doped Polymers on Polymers Loaded with Small Particles of Semiconductors, A. J. Heeger

The Use of Ternary Alloys to Passivate III-V Semiconductor Surfaces, G. S. Kino

Replamineform Transducers, L. W. Cross, J. V. Biggers and R. E. Newnham

Effects of Ledges and Other Defects on Surfaces of III-V Semiconductors, J. P. Hirth

The Electron Affinities for S_2 Molecules for One and for Two Electrons, J. L. Margrave

The Electron Affinity of Nitrogen Atoms for Three Electrons, J. L. Margrave

Taylor Instability of an Elastic-Plastic Solid, D. C. Drucker

Some Very Approximate Considerations of Penetration Mechanics for Normal Impact, D. C. Drucker

On the Failure of Ellipticity and the Emergence of Discontinuous Deformation Gradients in Finite Elastostatics, Eli Sternberg

Means for Low Expansion, E. E. Hucke

Metal Overlays on Large Optical Mirrors, J. P. Hirth

Note on Effect of Moderate Porosity on a Structure Index, B. Budiansky

Mechanisms of Low Coefficient of Expansion in ULE Glass, H. Reiss and J. L. Katz

Solid Phase Nucleation in Rapid Solidification Processes, H. Reiss and J. L. Katz

Theory of Local Electronic Structure, W. Kohn and A. Yariv

A Bond Change Model for the Electrooptic Effect, A. Yariv

The Influence of Electrons on the Structure of Very Strong Shocks in Metals, N. Bloembergen

Resistance to Shock Front Propagation in Solids, J. J. Gilman

Estimated Stability of Ternary Ionic Solids, J. L. Margrave

Investigation of the Homogeneous Fluorine Reactions by Modulative Molecular Beam Mass Spectrometry, A. Machiels and D. R. Olander

Antenna Structure for Near Millimeter and Infrared Diodes, P. L. Richards and A. Yariv

Some Microstructures Developed in 303 Stainless Steel Which Have Been Shock Loaded to the Megabar Range, D. J. Sandstrom and T. I. Jones

A Portable, Rechargeable System for Storage, Transportation and Production of Elemental Fluorine, J. L. Margrave

A Brief Note on Parameters for Correlating Penetration Problems, F. A. McClintock

The Effect of Electrolyte on Dipole Layers at Liquid-Air Interfaces, W. Madden, R. Gomer and M. Mandel

ON THE ESTIMATION OF A CRACK FRACTURE PARAMETER BY LONG-WAVELENGTH SCATTERING

B. Budiansky and J. R. Rice

ABSTRACT

On the basis of long-wavelength, far field scattering of elastic waves, an estimate is madc of the fracture-mechanics parameter $k_I = (k_I)max/\sigma$ associated with a flat crack. Here k_I is the mode I stress intensity factor associated with a flat crack, and $(k_I)max$ is the largest value of k_I along the crack perimeter. On the assumption that the location of the crack is known, three output measurements for a given input appear sufficient to estimate the orientation of the plane of the crack as well as k_I.

AN INTEGRAL EQUATION FOR DYNAMIC ELASTIC RESPONSE OF AN ISOLATED 3-D CRACK

B. Budiansky and J. R. Rice

ABSTRACT

By use of a steady state ($e^{-i\omega t}$) dynamic elastic representation theorem for fields created by relative motions ΔU_k on the faces of a crack, we reduce the problem of steady state response of an isolated three-dimensional planar crack, loaded by tractions on its surfaces, to an integral equation for ΔU_k.

THERMODYNAMICS OF THE QUASI-STATIC GROWTH OF GRIFFITH CRACKS

J. R. Rice

ABSTRACT

Restrictions on the quasi-static extension, or healing, of Griffith cracks are developed in the framework of irreversible thermodynamics. It is emphasized that thermodynamics requires that $(G-2\gamma)\dot{\ell} \geq 0$, where $\dot{\ell}$ is crack speed, G the Irwin energy release rate, and 2γ the work of reversible separation of the surfaces to be fractured. Implications for "lattice trapping" models of cracks and for thermally activated crack motion are discussed, as are the effects on crack growth and healing of a surface-reactive environment, in which case γ must be given a definition appropriate to absorption-altered surface properties.

DETECTION OF SURFACE CRACKS BY LASER DOPPLER IMAGING OF ACOUSTIC WAVE PATTERNS

P. L. Richards and R. Gomer

ABSTRACT

It is proposed to investigate surface cracks by producing an optical image of standing wave patterns produced by acoustic wave scattering from such cracks. The method of producing this optical image consists of scanning the surface in a raster pattern with a focussed laser beam. A portion of the diffusely scattered laser light is imaged on a square law detector and there combined with a frequency shifted portion of the direct laser beam. The resultant ac signal corresponding to the sum or difference frequency of the Doppler shifted reflected and Bragg-shifted direct laser beam is then converted to ac, its amplitude synchronized with the raster and displayed. Thus a visual image of the acoustic amplitude over the surface is produced by utilizing the Doppler shift of laser light reflected from the acoustically excited surface. It is estimated that required sensitivity and signal to noise for rapid display are attainable with existing technology.

RADIANT ENERGY DISSIPATION IN CRACK PROPAGATION

J. R. Rice

ABSTRACT

It is pointed out that heterogeneity of fracture resistance on a small scale leads to an apparent work of fracture that includes not only the actual work absorbed in separation, but also radiant energy dissipation in the form of elastic deformation waves. An analysis of the process has been based on Freund's equations of unsteady crack motion, assuming an irregular one dimensional variation of the fracture resistance along the path of crack motion. Radiant losses are found to be greatest for macroscopically quasi-static crack growth and to diminish toward zero as the macroscopic crack speed approaches the limiting wave speed (Rayleigh speed for plane strain).

A SIMPLE METHOD OF DETECTING SURFACE CRACKS

R. Gomer

ABSTRACT

A simple method for visualizing surface cracks is presented. It consists of covering the surface with a liquid film and lowering the pressure so that gas contained in cracks expands and forms bubbles in the film which can be detected visually or by simple optical scanning. Crack volumes $>10^{-10}cm^3$ should be readily detectable; sensitivity can be controlled by choosing appropriate pressure ratios. The criteria for liquid not entering the crack and for stability of the external bubbles are given. By suitable choice of the viscosity and hence diffusion coefficient of the liquid, it is possible to either develop bubbles by diffusion of gas from supersaturated liquid to existing bubbles, or to prevent this.

AN INQUIRY INTO THERMOGRAPHIC DETECTION
OF SURFACE CRACKS

R. Gomer and F. A. McClintock

ABSTRACT

It is concluded that acoustic excitation of surface cracks, empty or liquid filled, does not produce enough heat to give rise to an easily detectable temperature rise near the crack.

DYNAMIC FRACTURE CRITERIA FOR IMPACT PROBLEMS

A. G. Evans

ABSTRACT

Recent theoretical results on the interaction of dynamic tensile stresses with cracks provide a basis for defining some preliminary brittle fracture criteria for insertion into computer codes. In particular, an energy criterion frequently used in these programs $\int \sigma^2 dt$, is shown to afford a useful description of the fracture threshold. However, contrary to present practice, the crack extension above the threshold is characterized by a different criterion (which exhibits a much stronger dependence on the pulse duration).

SOLID SOURCES FOR ELEMENTAL FLUORINE

J. L. Margrave

ABSTRACT

Production and storage of elemental fluorine as needed in a laboratory or field situation from a light-weight, inexpensive, rechargeable source would appear to be achievable by making use of reactions like

1. $HgF_2 + 2\ MF_6 = Hg(MF_6)_2 + F_2$
2. $AgF + 2\ MF_6 = AgMF_6 + \frac{1}{2}F_2$
3. $ZnF_2 + 2\ MF_6 = Zn(MF_6)_2 + F_2$

The thermodynamic driving force is the high electron affinity of the MF_6 molecule (M = Mo, W, Pt, U, etc.) which exceeds that of fluorine atoms so that the general reaction

4. $F^- + MF_6 = MF_6^- + F(\text{or } F_2)$

is allowed and should proceed smoothly at moderate temperatures.

Also, reactions like

5. $NOF + MF_6 = NOMF_6 + \frac{1}{2}F_2$
6. $SOF_2 + MF_6 = SOMF_6 + F_2$
7. $3NaF + UF_6 = Na_3UF_7 + F_2$

are possibilities although, not all of these reactions will be easily reversed for recharging of the fluorine source. The estimated temperatures for recharge reactions at 1-20 atm of

fluorine are in the range of 200-500C.

Aluminum containers or various Ni-alloys should be adequate for use with F_2 up to 500C and thus excessive weights of high-pressure steel cylinders can be avoided.

HIGH TEMPERATURE KINETICS OF REFRACTORY METAL
GASIFICATION BY ATOMIC FLUORINE

P. C. Nordine

ABSTRACT

Intrinsic kinetics for the F/Ir, Pt, Ta reactions were measured using microwave discharge, low pressure, transonic flow reactor techniques with filament gasification rates deduced from specimen resistance vs time measurements. Data were obtained in the temperature ranges 1000-1450K for Ir, 600-1430K for Pt and 1100-3030K for Ta, at F-atom partial pressures between 0.65-7.4 Pa. Also, transient filament resistance and temperature changes could be observed which lead to the conclusion that condensed fluoride films occur on the metals upon exposure to atomic fluorine. These films do not inhibit the gasification reaction. The F/Pt data at $T > 800K$ and the F/Ir data agree within experimental error with kinetic models which assume a reactant pressure independent F-atom sticking coefficient and competitive first order F-atom desorption, n-th order (in the F-atom surface concentration) product molecule desorption. Third order F/Ir and second, fourth order F/Pt kinetics suggest $IrF_3(g)$, $PtF_2(g)$ and $PtF_4(g)$ are in the major produce species. Quasi-equilibrium pre-exponential rate

law parameters based on these species agree with those derived from the rate measurements. At lower temperature the F/Pt reaction is zero-order in the incident F-atom flux. The F/Ta kinetics are qualitatively similar to the F/Ir, Pt kinetics but reaction persists to much higher temperature and non-integral reaction order is obtained at the highest temperatures. A quantitative model of the F/Ta reaction kinetics is not proposed. However, a disagreement between measured rates of Ta gasification and those predicted by the Machiels and Olander model of F_2/Ta kinetics is found, which suggests a change in reaction mechanism between their experiments, at $P_{F_2} < 10^{-2}$ Pa and the present results obtained at $P_F > 0.6$ Pa. Instructive comparisons are made between the results obtained for these and the F/W, Mo, Ti systems and the implications of quantitative results from F/Ir, Pt models are discussed.

STABILITIES AND HIGH TEMPERATURE PROPERTIES
OF REFRACTORY OXYNITRIDES

J. L. Margrave

ABSTRACT

The stabilities and various thermodynamic properties of several refractory oxynitrides - Si_2ON_2, $SiAlO_2N$, Al_3O_3N, etc., have been calculated on the basis of an ionic model and various available synthetic data*. In general, the oxynitrides are more stable than the corresponding nitrides, are more oxidation resistant and possess high melting points. Decomposition to yield oxides plus gaseous nitrogen is expected to be the predominant reaction at high temperature in vacuum or in oxidizing atmospheres. The results indicate:

(a) $\Delta H^\circ_{f,298}$ [Si_2ON_2(solid)] = -300 ± 50 Kcal mole^{-1}

S°_{298} [Si_2ON_2(solid)] = 20 ± 2 Cal deg^{-1} mole^{-1}

(b) $\Delta H^\circ_{f,298}$ [$SiAlO_2N$(solid)] = 120 ± 50 Kcal mole^{-1}

S°_{298} [$SiAlO_2N$(solid)] = 14 ± 2 Cal deg^{-1} mole^{-1}

Ionic model calculations are also applicable to solids like $MgSiN_2$, LiSiNO, $LiSi_2N_3$ and to $\frac{1}{2}Si_3O_3N_4$, Y_3O_3N, etc., which form exothermically from the corresponding binary oxides/nitrides.

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*See (1) K. H. Jack, J. Materials Science 11, 1135 (1976).
(2) S. Umebayashi and K. Kobayashi, Bull. Amer. Cer. Soc. 56, 578 (1977).

THE STABILITIES OF REFRACTORY OXYFLUORIDES

J. L. Margrave

ABSTRACT

The stabilities of several refractory oxyfluorides* - AlOF, ScOF, YOF, LaOF, CeOF - have been calculated on the basis of an ionic model and their structures, which are closely related to the fluorite structure, as summarized in the table. The results indicate that these ternary compounds are stable with respect to thermal dissociation at temperatures up to at least 2000K. The attack of elemental fluorine on these materials is thermodynamically allowed but is likely to be kinetically slow.

Predicted Properties of Refractory Oxyfluorides

	$\Delta H^\circ_{f,298}$ Kcal mole^{-1}	S°_{298} Cal deg^{-1} mole^{-1}
AlOF	-305±30	9±1
ScOF	-275±30	14±2
YOF	-293±30	16±1
LaOF	-282±30	19±1
CeOF	-314±30	20±1

*For syntheses and structures see:

(1) W. H. Zachariasen, Acta Cryst. 4, 231 (1951).

(2) W. Finkelnburg and A. Stein, J. Chem. Phys. 18, 1296 (1950).

(3) N. Baenziger, J. Holden, G. Knudson and A. Popov, J. Am. Chem. Soc. 76, 4734 (1954).

THE STABILITIES OF GROUP-IV NITRIFLUORIDES

J. L. Margrave

ABSTRACT

The nitrifluorides of Group-IV transition metals* appear to be attractive refractory compounds for use at high temperatures and in fluorine atmospheres. Thermodynamic stabilities have been calculated on the basis of an ionic model and the known fluorite-like structures for TiNF, ZiNF, HfNF, ThNF and UNF, as summarized in the following table.

Predicted Properties of Refractory Nitrifluorides

	$\Delta H^\circ_{f,298}$ Kcal mole^{-1}	S°_{298} Cal deg^{-1} mole^{-1}
TiNF	-130±20	24±2
ZiNF	-170±20	20±2
HfNF	-200±30	18±2
ThNF	-200±30	16±2
UNF	-200±30	16±2

*For syntheses and structures see:

(1) R. Juza, R. Sievers and W. Jung, Naturwissensch. 53, 551 (1966).

(2) R. Juza and R. Sievers, Z. Anorg. Allgem. Chem. 363, 258 (1968).

(3) W. Jung and R. Juza, *ibid*., 399, 129 (1973).

(4) W. Jung and R. Juza, *ibid*., 399, 148 (1973).

THE CONSOLIDATION OF POWDERS

Analysis of Processing - Structure - Property Relationships

Alan Lawley

ABSTRACT

The mechanical behavior and property integrity of consolidated metal powders are considered with emphasis on fully-dense material for high-performance applications. Observed correlations between mode of consolidation, microstructure and properties are understood by analysis of the form of pore closure accompanying densification. In powder forging, a rational approach is outlined for determination of the processing parameters necessary to achieve full density without cracking and with property levels equal to or better than those of conventional forgings. It is found that full density is not a sufficient criterion to guarantee integrity vis a vis dynamic properties (e.g., toughness, fatigue). Rather, the mode of consolidation is a further critical factor; in general, lateral flow of material must accompany densification to enhance dynamic property levels. Available consolidation-structure-property correlations pertain to powders solidified at rates below $\sim 10^4\,°C/s$.

ADVANCES IN SOLIDIFICATION PROCESSING

Robert Mehrabian

ABSTRACT

Our current understanding of the relationship between heat flow and solidification structure is reviewed in rapid solidification processes; atomization, splat cooling and surface layer melting. Emphasis is placed on limitations in attainable heat transfer coefficients during powder production and splat cooling. Calculations are presented to show the relationship between absorbed heat flux and the important melting and solidification variables affecting crystalline structures during laser surface melting of aluminum, iron and nickel. It is noted that data relating dendrite arm spacings to average cooling rate during solidification is only available in a few alloy systems. During dendrite solidification, local solidification time in the mushy zone gives a better indication of time available for coarsening phenomena to occur than average cooling rate. Recent evidence indicates that substantial undercoolings are achieved during certain rapid solidification processes. This undercooling affects the structure and segregation patterns of alloys in ways that cannot be directly correlated to dendrite arm spacing and normal non-equilibrium segregation patterns.

ON THE SIGNIFICANCE OF SUPERPLASTIC FLOW
IN HOT ISOSTATIC CONSOLIDATION OF
RAPIDLY SOLIDIFIED ALLOYS

R. L. Coble

ABSTRACT

A brief review of the properties of superalloys in comparison with the temperatures and pressures achievable in commercial HIP apparatus indicates that the yield stresses can be easily exceeded for all alloys. Thus, a major component of consolidation must take place by plastic flow. However, complete densification is precluded by plasticity, as indicated by the models for deformation of thick-walled shells. A question being examined is whether the transition to microplastic modelling will give a different result for the density limit than the continuum models. After plastic compaction is complete, creep controlled by dislocation climb, or superplastic flow will give time dependent densification, but the models indicate that the rate would drop to zero asymtotically as theoretical density is approached. Hence, densities less than theoretical are predicted by these models. Densification by lattice or grain boundary diffusion have no such limit, the rate is predicted to be finite as the density approaches the theoretical value. Thus, higher pressures in processing, or the occurrence of superplastic

flow can appreciably shorten the times required for complete densification, but are not necessary for HIP to theoretical density. The insertion of a field for superplastic flow in a deformation map for nickel was developed to show the extent to which advantage is gained in shortening the time required for consolidation in HIP. It is to be noted that the total strains required in hot pressing or hot isostatic pressing are relatively small (<0.5) and compressive loading precludes generalized cracking. For other processes, (extrusion or injection molding or forging into a die cavity) in which extensive deformation of blanks occurs with biaxial tensile stresses in the expanding (free) surfaces, superplastic flow is viewed as essential.

FRACTURE RESISTANCE IN HIGH-STRENGTH
ALUMINUM ALLOYS BY POWDER METALLURGY PROCESSING

W. L. Otto, Jr.

ABSTRACT

The present discussion will detail the application of powder metallurgy technology to high strength and elevated temperature aluminum alloys. In addition, a brief discussion of aluminum powder atomization techniques and future developments in aluminum powder metallurgy will be presented.

OBSERVATIONS ON RSP RESEARCH AS APPLIED
TO HIGH-STRENGTH STEELS

M. Cohen

ABSTRACT

The application of rapid solidification methods to heat-treatable (martensitic) steels seems particularly attractive from the standpoint of attaining a fine grain size and well-distributed carbides in the final tempered martensite. However, it is important that potential experimental difficulties be kept in mind, which may otherwise obscure the benefits being sought. Some early experience in this connection shows that the consolidation steps play a key role in the ultimate structure/property relationships, and so the RSP powders must be available in sufficient amounts to optimize the subsequent deformation-processing for producing the bulk materials.

CAN NDE INFER THE MATERIALS PROPERTIES OF DEFECTS

R. M. Thomson and G. S. Kino

ABSTRACT

Some qualitative comments are made regarding possibilities for studying the material properties of real cracks over and above the purely geometrical results one obtains from crack imaging by ultrasonics. Possibilities are discussed for studying the opening at the tip of crack-like defects and for measuring the stresses near such defects.

SCATTERING OF LONG WAVE LENGTH SOUND WAVES FROM LOCALIZED DEFECTS IN SOLIDS

W. Kohn and J. R. Rice

ABSTRACT

It is shown that all observable long wavelength scattering information about a defect in a given isotropic matrix is contained in 22 independent parameters. One of these is the mass excess δM which can be unambiguously derived from scattering data. The other 21 are the independent matrix elements of a fourth rank tensor $D_{ijk\ell}$ which is symmetric under interchange of i and j, of k and ℓ, and of (oj) and (kℓ). All 22 parameters can be obtained from measurements in which longitudinal waves are incident and only scattered longitudinal waves are measured. Thus no additional information can be obtained from either incident or scattered transverse waves (although there may be practical reasons for using them). A useful quantity is the partially contracted symmetric tensor $D_{mn} \equiv D_{iimn}$, which can be brought into one-to-one correspondence with either an elliptical void or an elliptical, infinitely stiff inclusion. A general limitation is that long wavelength measurements determine only quantities of the form $\Delta c \cdot L^3$, where Δc is the change of an effective stiffness coefficient and L is a characteristic

length. They cannot, without additional information, separately determine Δc and L^3. However the effective $|\Delta c|$ is never much larger than the stiffness of the matrix (even for an infinitely stiff inclusion) so that some rough bounds on L can still be obtained. A crack can be identified from the fact that $\delta M = 0$. Two examples, a spherical defect of arbitrary bulk modulus K and a circular crack, are worked out.

A COMPARISON OF INVERSE METHODS IN THE
HIGH FREQUENCY LIMITS AND IMAGING TECHNIQUES
FOR NON-DESTRUCTIVE EVALUATION

G. S. Kino

ABSTRACT

Bleistein in a report and in a talk at the MRC demonstrated how Fourier inversion techniques, first employed in electromagnetic theory, can be applied to the non-destructive evaluation problem.* In his examples he makes use of a simple scalar wave equation.

We have extended the method to deal with solid media. We show that it is possible to reduce the problem of determining the definition of the method, to that of finding the definition of a physical point in space. Following Bleinstein's technique of Fourier transformation, we find that for a complete aperture (2π) and excitation by a plane wave source of wave number k, a two dimensional reconstruction yields a scattering amplitude $J_o(kR)$ where R is the distance from the original imaging point. On the other hand a reconstruction using the back scattered signal to the point of excitation yields an amplitude variation $J_o(2kR)$, i.e., better definition by a factor of 2.

If, in addition, we carry out a frequency transformation corresponding to varying from $k = 0$ to ∞, the point is recon-

structed as a δ function. But a limited range of k once more limits the definition and, in some cases, may yield poorer definition than using only one frequency (one value of k) with a full aperture.

A comparison with imaging techniques shows that basically the imaging method is merely a hardware implementation of Fourier transform techniques. The use of a single frequency signal gives rise to the same definition as in the Bleistein case. Both cases also give the same results when the aperture is finite. For small apertures, as would be expected, the definition perpendicular to the central acoustic beam axis is controlled by the aperture angle, and the definition along the central axis is relatively poor.

Carrying out the transformation in k is another matter. Now the equivalent operation on an imaging system is to pulse the acoustic beam. As the amplitudes of the different Fourier components now depend on the nature of the applied pulse, the results obtained are different from those of the Bleistein technique.

A start has been made on determining how these techniques can be used to measure material parameters as well as the shape of a flaw. The indications are that the amplitude of the signals obtained depend on the amplitudes of the discontinuities in acoustic impedance at the flaw surface as well as its curvature. As the curvature of the flaw surface can be measured independently by this technique, the implication that the acoustic

impedance of the flaw can be determined both by imaging techniques and by the Bleistein inversion procedure.

*N. Bleistein and J. K. Cohen, "Application of a New Inverse Method to Non-Destructive Evaluation", Final Report for Rockwell International Corporation, MS-R-7716, Mathematics Division, Denver Research Institute, University of Denver.

SOME COMMENTS ON THE APPLICATION OF GEOMETRICAL DIFFRACTION THEORY TO ELASTODYNAMIC PROBLEMS

J. D. Achenbach

ABSTRACT

Some general results for diffraction of longitudinal waves are given. Primary diffracted body waves, diffracted surface waves, reflection of surface waves, and body waves generated by diffraction of surface waves are treated.

THE STRENGTH OF OPTICAL FIBERS

A. G. Evans

ABSTRACT

The utilization of long lengths of optical fibers is presently limited by fiber fracture. Much progress has recently been demonstrated in the reduction of "low-strength" failures emanating from extrinsic flaws. Further progress is anticipated, and strength limited by the "high-strength" population (especially after proof testing) can be confidently anticipated. A further enhancement of fiber performance will, thereafter, be predicated on the ability to modify the "high-strength" population.

To estimate the feasibility of such an undertaking, calculations have been performed to determine whether the present high strength regime represents the intrinsic strength of the fibers. The calculations consider foreign ions (OH^-, Na^+, etc.) as network modifiers that act as fracture nuclei; and demonstrate that the present strengths could indeed be intrinsic network strengths in the presence of typical proportions of network modifiers. The high strength regime can only be translated, therefore, by eliminating moisture (or other sources of network modifiers) from the fiber preforms and the drawing environment,

and by hermetically sealing the fibers. The latter is the primary limitation. Hence, this study further emphasizes the need to seek out a metal coating that acts as a fully effective moisture barrier.

STATISTICAL INTERPRETATION OF FIBER-OPTIC STRENGTH DATA

F. A. McClintock

ABSTRACT

The high reliability desired in optical fibers puts a premium on the interpretation of tests on specimens of varying length, on detecting rare sources of low strength, on comparing bending and tensile tests, and on estimating the effect of slow crack growth on strength distributions. Statistical tests to help with these problems are presented and illustrated in this paper.

HIGH PERFORMANCE CERAMICS

A. G. Evans and R. L. Coble

ABSTRACT

The development of ceramics with optimum mechanical and optical properties is limited by the present constraints on microstructure control imposed by fabrication technology. Improved fabrication procedures that are capable of developing both the requisite microstructures and near-net shape components are thus explored. Liquid phase sintering based on an extended knowledge of phase equilibria and diffusion/reaction kinetics offers considerable potential, especially if precompaction of fine powders can be achieved by shock wave techniques. Chemical vapor deposition, with controlled nucleation to achieve equiaxed, fine grains also looks promising. In either case, shaping by high temperature superplastic forming techniques may be viable, depending on the grain boundary purities and the ratios of grain size to boundary diffusivity that can be achieved.

THE SUPPRESSION OF CAVITY FORMATION IN CERAMICS: EFFECTS ON SUPERPLASTICITY

A. G. Evans, J. R. Rice and J. P. Hirth

ABSTRACT

Ceramics exhibit macroscopic stress/strain rate relations that should lead to superplastic extension. However, premature fracture is normally encountered, due to the formation and growth of grain boundary cavities. Cavity nucleation and growth has thus been analyzed in an attempt to identify microstructures and/or strain rate regimes that would suppress cavity evolution and hence, allow superplasticity.

Accordingly, the stress concentrations that develop in ceramics - due to boundary sliding, elastic and thermal anisotropy, etc. - and their relaxation by diffusion have been estimated. It is demonstrated that for typical grain sizes and boundary diffusivities, these stress concentrations should not exceed the applied stress by more than ≃3 (2 is more typical). Then an analysis of cavity nucleation rates has indicated that there is a "critical" nucleation stress that depends primarily on the surface energy, and the boundary of interface energy. Combined with the stress concentration results, the nucleation analysis indicates that materials with "clean" grain boundaries

(no amorphous phase, no inclusions) should sustain applied stresses $\gtrsim$500 MPa without nucleating cavities. Hence, if the deformation rates at these stresses can be rendered sufficiently large by developing very fine scale microstructures ($\approx$0.1μm), superplastic deformation should be feasible. However, the presence of amorphous boundary phases and/or boundary inclusions and pores can greatly augment cavity nucleation, and lead to premature failure. The major emphasis for attaining superplastic ceramics should thus be concerned with the minimization of deleterious boundary entities.

ELASTIC CONTRIBUTIONS TO VOID NUCLEATION IN CERAMICS

J. P. Hirth

ABSTRACT

At elevated temperatures the role of vacancy supersaturation in promoting void nucleation is well understood. The possibility that elastic strain energy enhances nucleation has been suggested by Rajand Ashby and others. The magnitude of the effect is determined here and found to be negligible for the case of nucleation within a grain, but of importance in void growth to sizes larger than 0.1μm in void diameter. The results indicate that the effect will be of little importance for the case of nucleation at grain boundaries also.

SUGGESTION FOR A MOLECULAR RESONANCE FREQUENCY STANDARD

W. H. Flygare

ABSTRACT

We propose to use a Fabry-Perot cavity filled with a heavy molecule at low pressure to generate a narrow rotational resonance line within the cavity spectral response to stabilize a solid state oscillator from 20-50 GHz. Further narrowing of the resonance can be achieved by driving the transition into saturation to produce a narrow Lamb dip. The details of the device are given. The solid state oscillator which is phase stabilized to a molecular resonance transition is then capable of stabilizing a quartz oscillator by direct comparison with a high harmonic of the quartz system.

THE RESISTIVITY OF METALLIC LIQUIDS AND GLASSES

H. Ehrenreich

ABSTRACT

The correspondence between the electrical properties of amorphous metals and liquids having the same composition, at the melting point, suggests that the appropriateness of the Ziman-Faber theory should be further investigated. A set of mutually consistent calculations for liquid Fe, Co, Ni, and Cu yield results that are in rather poor agreement with experiment, the mean free paths being smaller than the interatomic distance. This is taken to be a reflection of the fact that the positional correlations of the atoms are seriously underestimated . The good agreement obtained in previous calculations by the Bristol group is an artifact of the extraordinary sensitivity of the resistivity to Fermi surface parameters. For CoP, the Ziman-Faber formula overestimates the resistivity by about a factor of three. The resistivity contribution of the metalloid is small due to its weak scattering strength. The transport properties are relatively insensitive to the appreciable metalloid-metal short range order that probably exists in these materials.

THEORETICAL STRENGTH AND
EFFECTIVE FORCE LAWS FOR ATOMS IN METALS

H. Ehrenreich and R. M. Thomson

ABSTRACT

Recent ab initio band structure calculations for transition metals in which one of us participated have yielded results for the cohesive energy of the solid as a function of lattice parameter. We have used these results to calculate the theoretical "strength" of the solid against a negative pressure with satisfactory results. We have compared this result with calculations of the theoretical strength using extant empirical force law for Cu, and find important short comings. Comments are made about how one might generate an adequate force law for such "defect" calculations based on an adequate theoretical foundation of the electronic structure of solids.

MICROWAVE AND INFRARED COATINGS FROM DOPED POLYMERS OR POLYMERS LOADED WITH SMALL PARTICLES OF SEMICONDUCTORS

A. J. Heeger

ABSTRACT

The potential use of polymer coatings as microwave and infrared absorbers is investigated. Two separate approches are considered for the generation of polymer coatings with the desired properties; addition of a volume fraction of semiconducting particles, or chemical doping of the polymer. The analysis implies that the desired result can be achieved; approximately 90% of the incident radiation can be absorbed. Although relatively thick coatings ($\sim$1mm) would be required at 35 GHz, thinner films would be adequate at higher frequencies. This technique would have broad bandwidth and would be easier and more efficient at higher microwave and infrared frequencies.

EFFECTS OF LEDGES AND OTHER DEFECTS
ON SURFACES OF III-V SEMICONDUCTORS

J. P. Hirth

ABSTRACT

The variability of optical and electronic surface properties of cleaved GaAs {110} surfaces and the changes of these properties with fractional monolayer adsorption of various species may be associated with surface ledge structure. The possibility that ledges are sites for creation of extrinsic surface states is discussed. Ledge structures on cleaved, and as grown crystal surfaces are also characterized.

THE ELECTRON AFFINITIES OF S_2-MOLECULES
FOR ONE AND FOR TWO ELECTRONS

J. L. Margrave

ABSTRACT

Solids containing the $S_2^{=}$ species are well-known but thermodynamic data are limited. Available information for FeS_2, TiS_2 and NiS_2 has been utilized, along with spectroscopic information on isoelectric species to calculate

$$E^1_{S_2} = 11 \pm 5 \text{ Kcal mole}^{-1}$$

$$E^2_{S_2} = 135 \pm 10 \text{ Kcal mole}^{-1}$$

Thermal stabilities for important layer-compounds like TaS_2, NbS_2, VS_2 and other refractory sulfides have been derived.

THE ELECTRON AFFINITY OF NITROGEN ATOMS FOR THREE ELECTRONS

J. L. Margrave

ABSTRACT

Thermodynamic and spectroscopic data have been utilized for calculating the electron affinity of nitrogen atoms for three electrons, i.e., the energetics of the reaction

$$N(gas) + 3e(gas) = N^{-3}(gas).$$

This ion is stabilized in ionic crystals like Li_3N, AlN, the alkaline earth nitrides and many of the transition metal nitrides. From data on more than 20 compounds, one derives

$$E_N^3 = 605 \pm 75 \text{ Kcal mole}^{-1}$$

from thermodynamic cycles.

Extrapolations of spectroscopic data for some iso-electronic species yields

$$E_N^2 = 230 \pm 50 \text{ Kcal mole}^{-1}$$

$$E_N^3 = 650 \pm 100 \text{ Kcal mole}^{-1}$$

These data have been used in calculations of stabilities for ionic crystals like MNF, $AlON_x$, Si_2ON_2, $SiAlO_2N$ and for transition metal oxynitrides.

ON THE FAILURE OF ELLIPTICITY AND THE EMERGENCE OF DISCONTINUOUS DEFORMATION GRADIENTS IN FINITE ELASTOSTATICS

Eli Sternberg

ABSTRACT

This investigation concerns equilibrium fields with discontinuous displacement gradients, but continuous displacements, in the theory of finite plane deformations of possibly anisotropic, compressible elastic solids. "Elastostatic shocks" of this kind, which resemble in many respects gas-dynamical shocks associated with steady inviscid flows, are shown to exist only if and when the governing field equations of equilibrium suffer a loss of ellipticity. The present work aims exclusively at the local structure of such equilibrium fields near a point on the shock-line. For this purpose it is sufficient to consider merely piecewise homogeneous electrostatic shocks, in which the shock-line is straight and separates two distinct homogeneous deformations (see Fig. 5). Particular attention is given to weak shocks and an example pertaining to a shock of finite strength is explored in detail. Also, necessary and sufficient conditions for the "dissipativity" of time-dependent equilibrium shocks are established. Finally, the relevance of this analysis to localized shear failures --

such as those involved in the formation of Lüders bands -- is discussed in terms of a bifurcation of an unstable homogeneous deformation into a piecewise homogeneous time-dependent elastostatic shock.

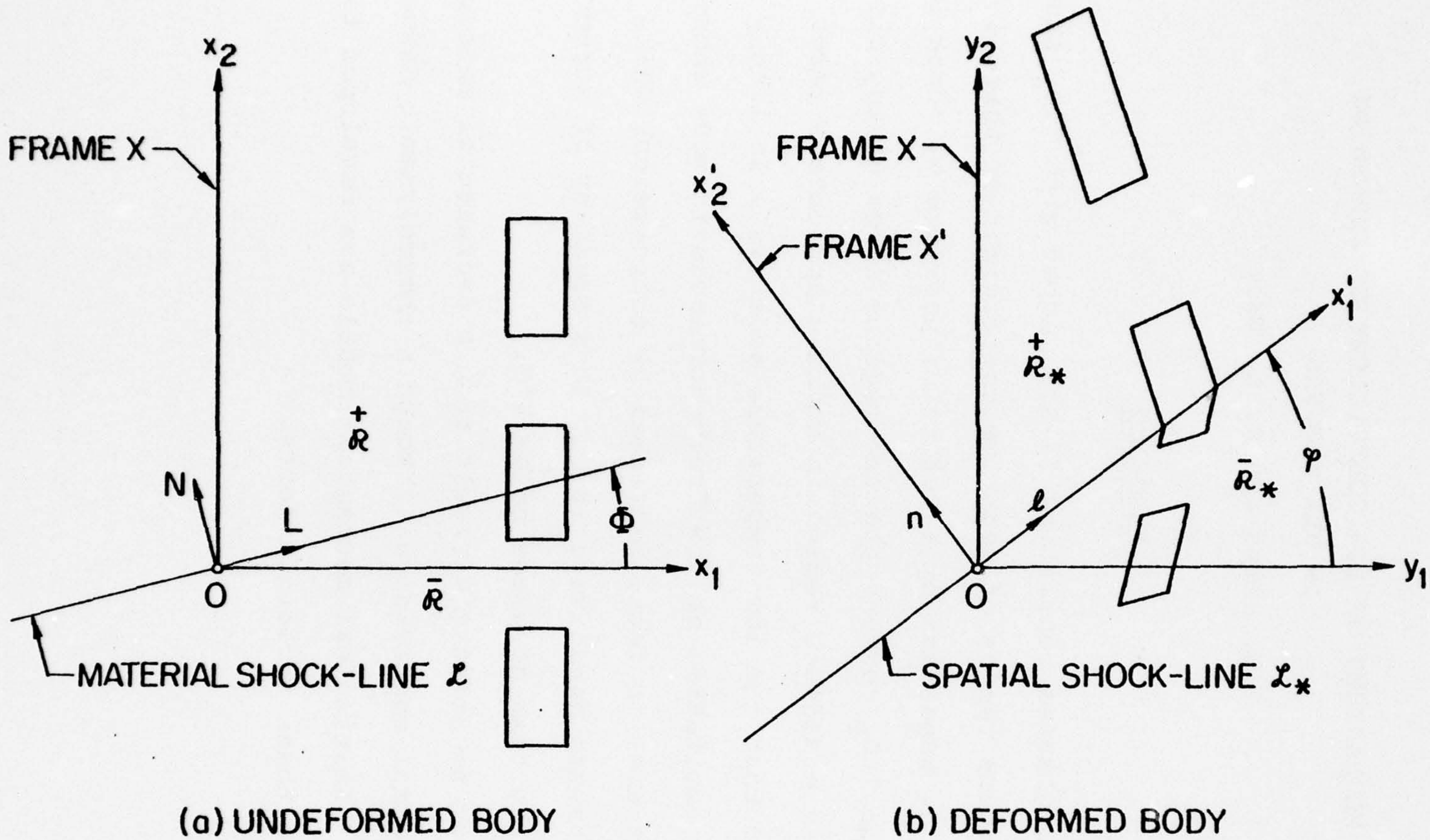

FIGURE 5. KINEMATICS OF PIECEWISE HOMOGENEOUS ELASTOSTATIC SHOCKS

MECHANISMS OF LOW COEFFICIENT OF EXPANSION IN ULE GLASSES

H. Reiss and J. L. Katz

ABSTRACT

ULE glasses consisting of SiO_2 doped with TiO_2 show two temperature ranges of negative coefficient of thermal expansion, α, separated by a region of positive α. Upon increasing the TiO_2 content the two regions merge giving rise to a flat intermediate region in which α approaches zero. It is shown that the low temperature negative α is likely due to the excitation of low frequency acoustic mode whose frequencies are, in fact, decreased by compression, while the high temperature negative α is due to a break-up of structure much like the case of water below 4°C.

Both negative α's result from a decrease of entropy upon isothermal compression (through a thermodynamic Maxwell relation). Statistical mechanical models are developed to demonstrate these various effects.

SOLID PHASE NUCLEATION
IN RAPID SOLIDIFICATION PROCESSES

H. Reiss and J. L. Katz

ABSTRACT

Transient nulceation has been studied for the nucleation of crystals in metal melts. The non-steady differential difference equations have been solved both for constant temperature and temperature decreasing linearly with time. The relaxation to the steady state is shown to be typically of the order of 10^{-13} sec., of the same magnitude as the fundamental "vibration" frequency in the liquid. This implies that in rapid solidification homogeneous nucleation will always occur at achievable cooling rates unless the solid liquid interfacial tension is abnormally high, and that other process, e.g., growth, must be responsible for the attainment of amorphous metals.

Assuming that the linear cooling rate is β°K sec^{-1}, the total number of nuclei produced per cubic centimeter in a given cooling run can be shown to be

$$N = \frac{1}{\beta} \int_{o}^{T_o} J(T)\,dT \qquad (1)$$

where J(T) is the steady state nucleation at temperature T and

T_o is the melting point. For copper this proves to be

$$N = \frac{2.42\times10^{40}}{\beta}\ \text{cm}^{-3} \qquad (2)$$

so that obviously unachievable cooling rates would be required to avoid nucleation. The use of the steady state value of J(T) in Eq. (1) is predicted on the prior knowledge that relaxation to the steady state is almost instantaneous. The small relaxation time stems ultimately from the low free energy of activation for diffusion in liquid metals.

THEORY OF LOCAL ELECTRONIC STRUCTURE

W. Kohn and A. Yariv

ABSTRACT

In connection with our studies of the electronic structure of interfaces we encountered the need for a theory of local electronic structure, whether the electronic wave functions themselves are delocalized or not. An appropriate quantity to focus on is the local density of states $n(\underset{\sim}{r},E)$ which, when integrated over E gives the electronic density $n(\underset{\sim}{r})$ at the point $\underset{\sim}{r}$, and when integrated over $\underset{\sim}{r}$ gives the density of electronic energy levels per unit energy, $n(E)$, for the entire system. We have developed a systematic method of determining $n(\underset{\sim}{r},E)$ which requires a knowledge of the Hamiltonian only in the vicinity of the point $\underset{\sim}{r}$. Numerical tests for the case of absolutely free electrons (which is the most unfavorable case) have given excellent results.

A BOND CHARGE MODEL FOR THE ELECTROOPTIC EFFECT

A. Yariv

ABSTRACT

The bond charge model used by Phillips and Van Vechten (PVV) in a dielectric description of bond ionicities has been used to derive an expression for the electrooptic coefficient (EO) in crystals. The total electrooptic coefficient is the sum of an electronic (rigid lattice) contribution and one due to the ionic displacement. The electronic contribution to the EO coefficient is related simply to the optical nonlinear constant of the crystal (i.e., to the second harmonic generation coefficient) and has been considered in the PVV framework by Levine. The present analysis concentrates on the ionic contribution to the EO effect. The result of this work is an expression for the EO coefficient which contains known bond parameters and linear dielectric constants.

It is hoped that this analysis can be helpful to the identification of promising candidates for electrooptic crystal growth.

ANTENNA STRUCTURE FOR NEAR MILLIMETER
AND INFRARED DIODES

P. L. Richards and A. Yariv

ABSTRACT

Efficient coupling of free space radiation at near millimeter and infrared wavelengths to diode detectors and mixers is necessary for practical systems applications of these devices. A discussion of this coupling problem appeared in the 1975 MRC Report. A revised and extended version of this paper will appear in the 1977 Report. It includes an analysis of the coupling problem, a discussion of an approximate solution to the problem which should be of value in the design of coupling structures, and a qualitative discussion of a number of potentially useful structures.

THE EFFECT OF ELECTROLYTE ON DIPOLE LAYERS AT LIQUID-AIR INTERFACES

W. Madden, R. Gomer and M. Mandel

ABSTRACT

Equations describing the effect of electrolyte on the potential of a dipole layer at a liquid-air interface are set up. Their numerical solution is briefly outlined and the results of the calculation are presented. Substantial screening results for strong potentials even at very low electrolyte concentrations (10^{-4} M). The calculated variation of the screened potential with electrolyte concentration for various assumed values of the unscreened potential (i.e., with no electrolyte present) can be compared with the experimentally obtainable variation and this allows an estimate of the unscreened potential actually present. The latter is estimated to be 50 millivolts in the case of H_2O, the surface being negative with respect to the bulk of the water phase. The disruption of the water dipole layer by reorientation of H_2O molecules by ions is estimated. The effect is important only at high electrolyte concentration (1 to 0.1 M) where it improves the fit of the experimental data to theory.